

AD-760 701

RESEARCH ON MOLECULAR LASERS

George J. Wolga, et al

Cornell University

Prepared for:

Office of Naval Research  
Advanced Research Projects Agency

15 April 1973

DISTRIBUTED BY:

**NTIS**

National Technical Information Service  
U. S. DEPARTMENT OF COMMERCE  
5285 Port Royal Road, Springfield Va. 22151

AD 760701

RESEARCH ON MOLECULAR LASERS

Semiannual Report -- 31 March 1973

Cornell University

Ithaca, New York 14850

Reproduced by  
NATIONAL TECHNICAL  
INFORMATION SERVICE  
U S Department of Commerce  
Springfield VA 22151

Sponsored by:

Advanced Research Projects Agency

ARPA Order No. 660

DDC  
RECEIVED  
MAY 29 1973  
B

DISTRIBUTION STATEMENT A

Approved for public release;  
Distribution Unlimited

UNCLASSIFIED

Security Classification

## DOCUMENT CONTROL DATA - R&amp;D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

Cornell University  
Ithaca, NY 14850

2a. REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

2b. GROUP

N/A

3. REPORT TITLE

STUDY OF MOLECULAR LASERS

4. DESCRIPTIVE NOTES (Type of report and inclusive dates)

Semiannual Report - 1973

5. AUTHOR(S) (Last name, first name, initial)

George J. Wolga  
Simon H. BauerRoss A. McFarlane  
T. A. Cool

6. REPORT DATE

April 15, 1973

7a. TOTAL NO. OF PAGES

22

7b. NO. OF REFS

8a. CONTRACT OR GRANT NO.

N00014-67-A-0077-0006

b. PROJECT NO.

9a. ORIGINATOR'S REPORT NUMBER(S)

N/A

c.

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned  
this report)

d.

N/A

10. AVAILABILITY/LIMITATION NOTICES

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Office of Naval Research

## 13. ABSTRACT

Research concerning molecular and chemical lasers was conducted in the following areas:

1. Measurement of V-V and V-R, T rates among hydrogen halide molecules and the temperature dependence of the energy transfer rates previously determined for HF, DF, HF/CO<sub>2</sub>, DF/CO<sub>2</sub> Systems.
2. Vibrational relaxation studies of CO<sub>2</sub> (00<sup>0</sup>1) in the pressure range 1-100 atm,
- 3a. Chemical laser studies of the reaction of atomic oxygen and acetylene,  
b. Computer modeling of the CS<sub>2</sub>-O<sub>2</sub> chemical laser system.  
c. Chemical laser studies of the reaction of C<sub>3</sub>O<sub>2</sub> with oxygen.
4. Experimental study of the relaxation of CO<sub>2</sub> (001) and HF(v=1) by collisions with H and F atoms.
5. Studies of the influence of vibrational excitations on the reaction rate of atom exchange reactions e.g., HF(v) + D<sub>2</sub> → HD + DF.

DD FORM 1473  
1 JAN 64

UNCLASSIFIED

Security Classification

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Molecular Lasers						
Chemical Lasers						
Vibrational Relaxation						
Energy Transfer						
Chemical Reaction Rates						
Vibrational Energy Transfer						

## INSTRUCTIONS

1. **ORIGINATING ACTIVITY:** Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization (*corporate author*) issuing the report.

2a. **REPORT SECURITY CLASSIFICATION:** Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2b. **GROUP:** Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. **REPORT TITLE:** Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. **DESCRIPTIVE NOTES:** If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. **AUTHOR(S):** Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. **REPORT DATE:** Enter the date of the report as day, month, year, or month, year. If more than one date appears on the report, use date of publication.

7a. **TOTAL NUMBER OF PAGES:** The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7b. **NUMBER OF REFERENCES:** Enter the total number of references cited in the report.

8a. **CONTRACT OR GRANT NUMBER:** If appropriate, enter the applicable number of the contract or grant under which the report was written.

8b, 8c, & 8d. **PROJECT NUMBER:** Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9a. **ORIGINATOR'S REPORT NUMBER(S):** Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9b. **OTHER REPORT NUMBER(S):** If the report has been assigned any other report numbers (*either by the originator or by the sponsor*), also enter this number(s).

10. **AVAILABILITY/LIMITATION NOTICES:** Enter any limitations on further dissemination of the report, other than those

imposed by security classification, using standard statements such as:

- (1) "Qualified requesters may obtain copies of this report from DDC."
- (2) "Foreign announcement and dissemination of this report by DDC is not authorized."
- (3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through \_\_\_\_\_."
- (4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through \_\_\_\_\_."
- (5) "All distribution of this report is controlled. Qualified DDC users shall request through \_\_\_\_\_."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. **SUPPLEMENTARY NOTES:** Use for additional explanatory notes.

12. **SPONSORING MILITARY ACTIVITY:** Enter the name of the departmental project office or laboratory sponsoring (*paying for*) the research and development. Include address.

13. **ABSTRACT:** Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as (TS), (S), (C), or (U).

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. **KEY WORDS:** Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, roles, and weights is optional.

## SEMIANNUAL REPORT

### Reporting Period

1 October 1972 -- 31 March 1973

- |     |                                       |  |
|-----|---------------------------------------|--|
| 1.  | ARPA Order                            | 660  |
| 2.  | Program Code Number                   | 0173-7-006252  |
| 3.  | Name of Contractor                    | Cornell University   |
| 4.  | Effective Date of Contract            | 1 October 1968   |
| 5.  | Contract Expiration Date              | 30 September 1973  |
| 6.  | Amount of Contract for Current Period | \$190,000  |
| 7.  | Contract Number                       | N00014-67-A-0077-0006  |
| 8.  | Principal Investigator                | Professor G. J. Wolga  |
| 9.  | Telephone Number                      | (607) 256-3962   |
| 10. | Project Scientists                    | Professor S. H. Bauer<br>(607) 256-4028<br><br>Professor T. A. Cool<br>(607) 256-3512<br><br>Professor R. A. McFarlane<br>(607) 256-4075 |
| 11. | Title of Work                         | RESEARCH ON MOLECULAR<br>LASERS  |

Sponsored by

ADVANCED RESEARCH PROJECTS AGENCY

ARPA Order No. 660

The views and conclusions contained in this document are those of the authors and should not be interpreted as necessarily representing the official policies, either expressed or implied, of the Advanced Research Projects Agency or the U.S. Government.



## 1.0 REPORT SUMMARY

During the period 1 October 1972 - 31 March 1973, the ongoing program concentrated on a number of research areas that were felt to be of significant and practical importance to the successful development of chemical and molecular laser technology. The principal areas of effort were: extension of the  $V \rightarrow V$  and  $V \rightarrow R, T$  studies in the hydrogen halide and  $\text{HF}/\text{CO}_2$ ,  $\text{DF}/\text{CO}_2$  laser systems; experimental studies of the vibrational relaxation of  $\text{CO}_2(00^01)$  at high pressure and over a wide temperature range; gain studies in the  $\text{C}_2\text{H}_2 - \text{O}_2$  chemical laser system; chemical studies of the production of  $\text{C}_3\text{O}_2$ ; experimental study of the  $\text{C}_3\text{O}_2 + \text{O}_2$  chemical laser system producing vibrationally excited  $\text{CO}$ ; experimental studies of the vibrational deactivation of  $\text{HF}/\text{DF}$ ,  $v = 1$ , and  $\text{CO}_2(00^01)$  states by collisions with  $\text{H}, \text{D}, \text{F}, \text{N}, \text{O}$ ; study of the effect of vibrational excitation in  $\text{HF}$  upon the atom exchange reaction

$$\text{HF}(v) + \text{D}_2 \rightarrow \text{HD} + \text{DF}.$$

In all cases the primary method was the execution of laboratory experiments designed to provide quantitative results followed by appropriate integration with theory. A detailed statement of results and state of progress will be found in the balance of the report.

## 2.0 VIBRATIONAL RELAXATION IN HYDROGEN HALIDES, HF-CO<sub>2</sub> AND DF-CO<sub>2</sub> SYSTEMS

Professor T. A. Cool

### 2.01 HF-HCl, HF-HBr, HF-HI, and HF-DF Systems

During the past several months our new high repetition pulsed laser facility has been employed in studies of vibrational relaxation processes with the laser-induced fluorescence method. Of primary concern have been those molecular systems of current interest for the development of chemical lasers. Several promising reaction mechanisms for such devices lead to the formation of vibrationally excited HF in the presence of HCl, HBr, HI, and DF molecules. We have determined the rate constants for energy transfer and deactivation in the HF-HCl, HF-HBr, HF-HI, and HF-DF systems at 300 and 350°K, typical temperatures for laser operation.

Table I summarizes these measurements.

The present results contribute to the growing study of data concerning vibrational relaxation of HCl, HBr, and HF mixtures which has revealed the importance of strong attractive interactions in causing efficient conversion of vibrational energy into rotational motion of the collision pairs. Several rate constants for the present systems exhibit a marked decrease with increasing temperature similar to that found for the self-deactivation rates of HF and DF in recent shock tube and laser-fluorescence studies.

## 2.02 HF, DF, HF-CO<sub>2</sub> and DF-CO<sub>2</sub> Systems

The temperature dependence of vibrational relaxation processes provides qualitative information concerning the nature of the intermolecular potential between collision pairs. Our new apparatus has enabled a complete study of the temperature dependence from 300 to 700°K for the vibrational relaxation processes of the HF, DF, HF-CO<sub>2</sub> and DF-CO<sub>2</sub> systems. The present results extend our previous measurements made at a single temperature of 350°K. <sup>(4)</sup>

The results of these measurements are summarized in Figures 1-3.

Figure 1 shows the temperature dependence of the rate constant  $K_{11}$  (sec<sup>-1</sup>Torr<sup>-1</sup>) for the self-deactivation processes

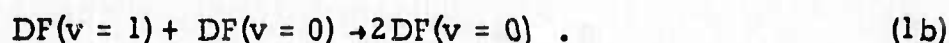
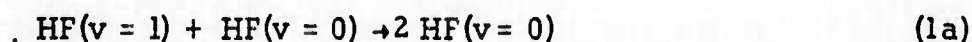
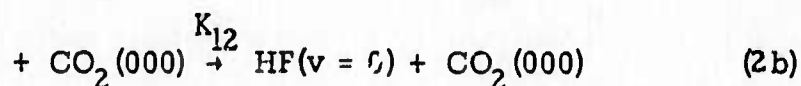
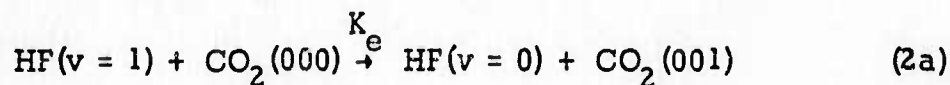


Figure 2 gives the observed variation with temperature of the rate constant sum,  $K_e + K_{12}$ , for the processes

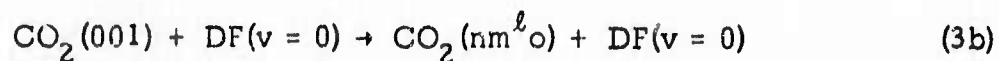
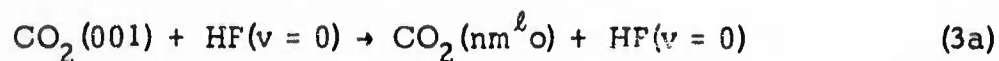


and the analogous processes for DF.

Figure 3 indicates the manner in which the rate constants for deactivation of the upper CO<sub>2</sub> laser level by HF and DF varies with



temperature by the process.



All of the measured rates exhibit a strong inverse dependence on temperature over the range investigated. This provides further evidence for a strong hydrogen-bonding interaction between HF(DF) and  $\text{CO}_2$ .

The results of the work summarized above have been submitted to the Journal of Chemical Physics for publication.

1. J. L. Abe and T. A. Cool, "Vibrational Relaxation in the HF-HCl, HF-HBr, HF-HI, and HF-DF Systems," to be published, J. Chem. Phys. June 15, 1973.
2. R. A. Lucht and T. A. Cool, "Temperature Dependence of Vibrational Relaxation in the HF, DF, HF- $\text{CO}_2$ , and DF- $\text{CO}_2$  Systems," in preparation for J. Chem. Phys.

TABLE I: SUMMARY OF MEASURED RATE CONSTANTS

SYSTEM	SYMBOL	T = 300K RATE CONSTANT (SEC <sup>-1</sup> TORR <sup>-1</sup> )	T = 350K $\Delta E_v$ (cm <sup>-1</sup> )	COLLISION NUMBERS, $Z_c$	PRODUCT OF VIBRATIONAL DIPOLE MOMENTS, $\mu_{HF} \mu_{HCl} \mu_{HBr} \mu_{HI} \mu_{DF}$ (DEBYE) <sup>2</sup>	SQUARED VIBRATIONAL MATRIX ELEMENTS (10 <sup>-40</sup> esu <sup>2</sup> cm <sup>2</sup> )
HF(1) + HF(0)	$k_{11}$	$7.0 \pm 1.0 \times 10^4$	$4.95 \pm 0.04 \times 10^4$	3962	73	96
HCl(1) + HCl(0)	$k_{22}$	$1200 \pm 300$	$900 \pm 200$	2886	5700	7500
HBr(1) + HBr(0)	$k_{22}$	$600 \pm 200$	$600 \pm 200$	2559	7920	7300
HI(2) + HI(0)	$k_{22}$	$4800 \pm 1000$	$3200 \pm 1000$	-81 <sup>a</sup>	1160	1590
DF(1) + DF(0)	$k_{22}$	$2.6 \pm 0.4 \times 10^4$	$1.8 \pm 0.3 \times 10^4$	2907	192	255
HF(1) + HCl(0)	$k_e + k_{12}$	$2.9 \pm 0.3 \times 10^4$	$2.2 \pm 0.3 \times 10^4$		213	260
	$k_e$	$1.6 \times 10^4 < k_e < 3.2 \times 10^4$	$1.2 \times 10^4 < k_e < 2.5 \times 10^4$	1076	193 < Z < 386	230 < Z < 480
	$k_{12}$	$< 1.6 \times 10^4$	$< 1.2 \times 10^4$	3962	< 386	< 478
HCl(1) + HF(0)	$k_{21}$	$2.0 \pm 0.3 \times 10^4$	$1.6 \pm 0.3 \times 10^4$	2886	309	359
HF(1) + HBr(0)	$k_e + k_{12}$	$7500 \pm 2000$	$3500 \pm 2000$		810	1500
	$k_e$	$4700 < k_e < 9500$	$2800 < k_e < 5500$	1403	650 < Z < 1300	950 < Z < 1850
	$k_{12}$	$< 4700$	$< 2800$	3962	< 1300	< 1850
HBr(1) + HF(0)	$k_{21}$	$1.6 \pm 0.3 \times 10^4$	$1.1 \pm 0.1 \times 10^4$	2559	380	475
HF(1) + HI(0)	$k_e + k_{12}$	$3500 \pm 2000$	$2000 \pm 1500$		1950	3170
HI(2) + HF(0)	$k_e' + k_{21}$	$1.95 \pm 0.25 \times 10^4$	$1.45 \pm 0.25 \times 10^4$	(b)	350	435
HF(1) + DF(0)	$k_e + k_{12}$	$13.3 \pm 1.0 \times 10^4$	$9.8 \pm 1.5 \times 10^4$		38	47.5
	$k_e$	$7.1 \times 10^4 < k_e < 14.3 \times 10^4$	$4.5 \times 10^4 < k_e < 11.3 \times 10^4$	1055	35.3 < Z < 71.5	41 < Z < 103
	$k_{12}$	$< 4.5 \pm 0.7 \times 10^4$	$< 3.3 \pm 0.5 \times 10^4$	3962	< 115	< 140
DF(1) + HF(0)	$k_{21}$	$4.5 \pm 0.7 \times 10^4$	$3.3 \pm 0.5 \times 10^4$	2907	115	140

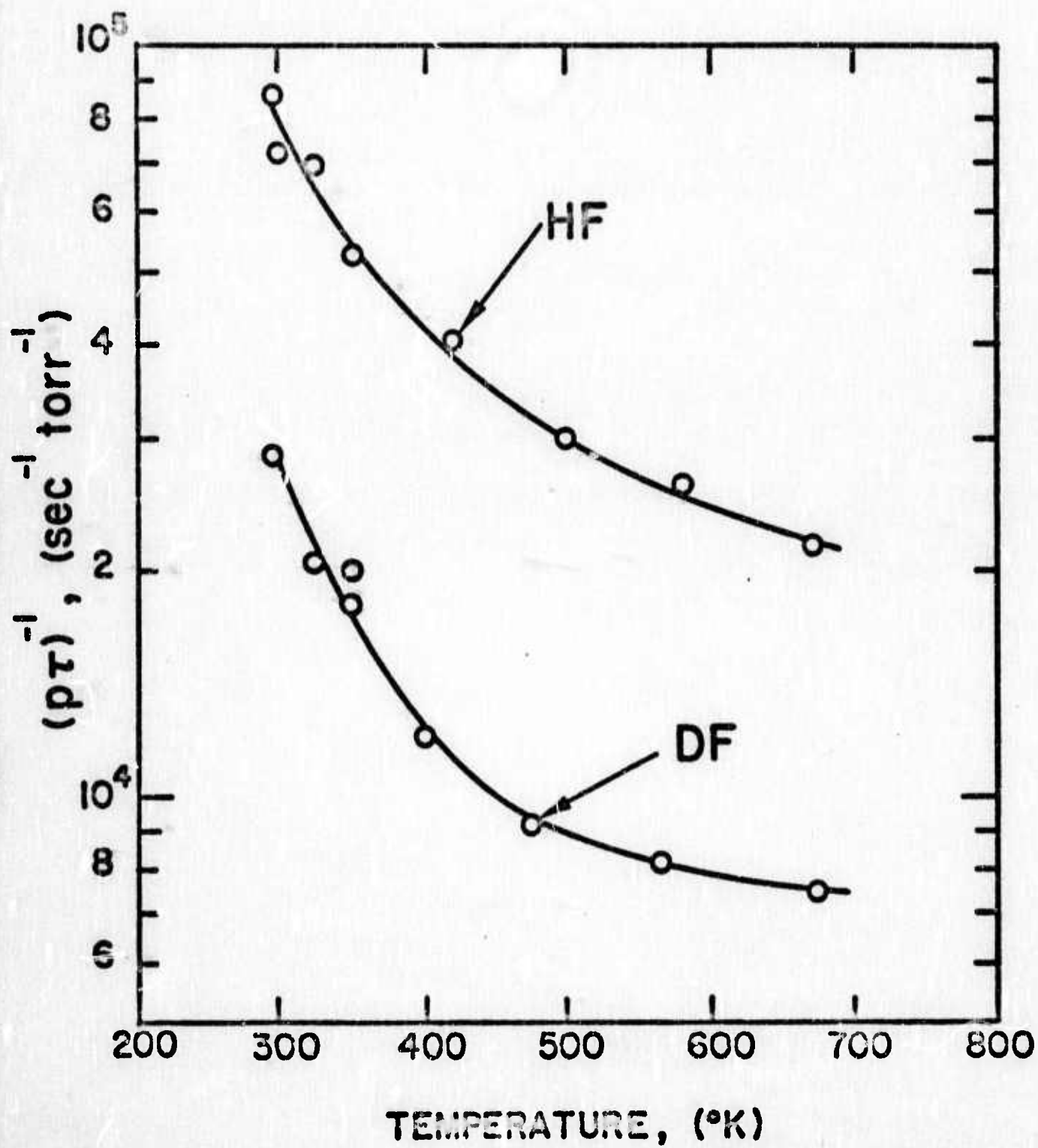


FIGURE 1

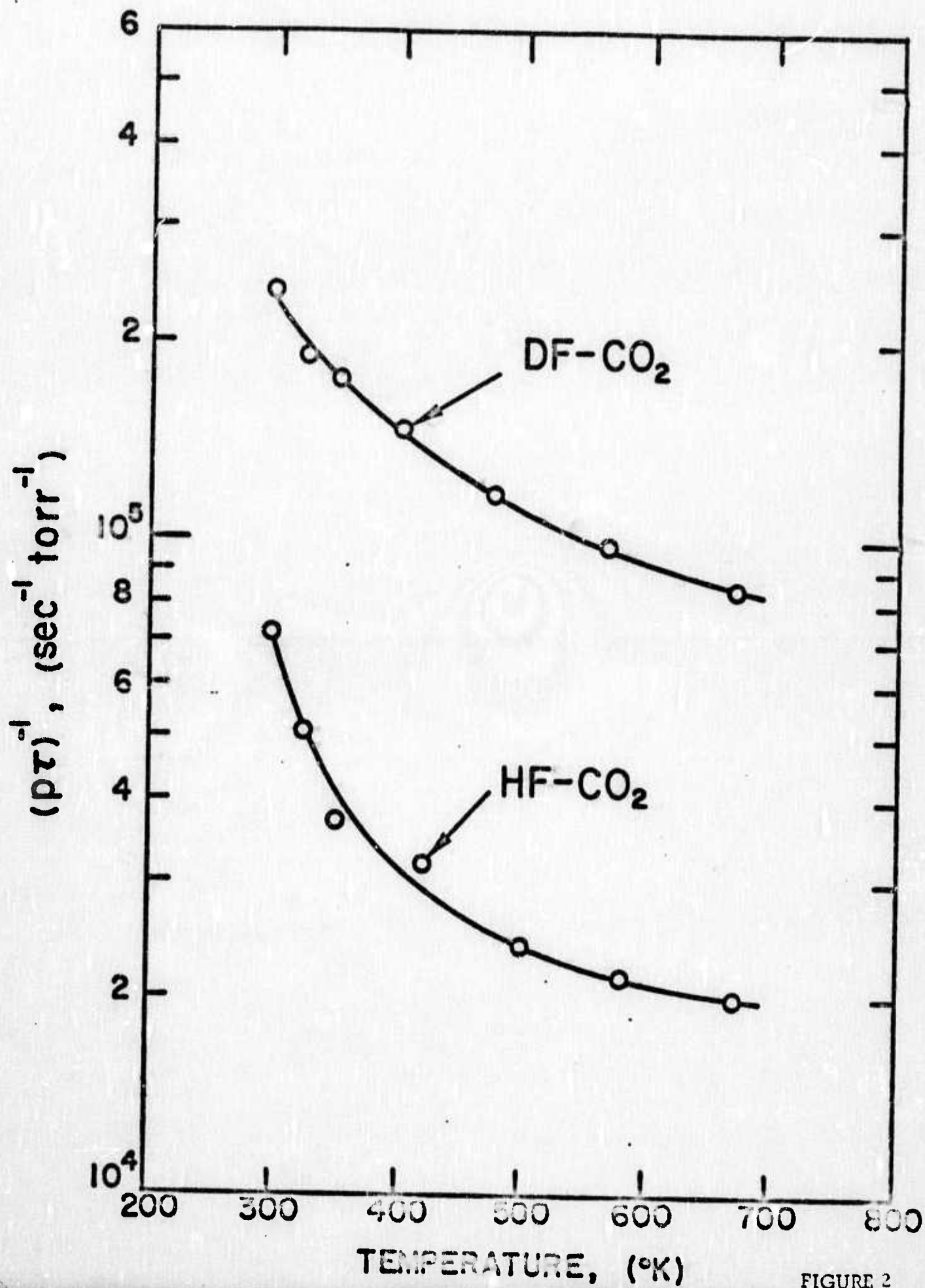


FIGURE 2

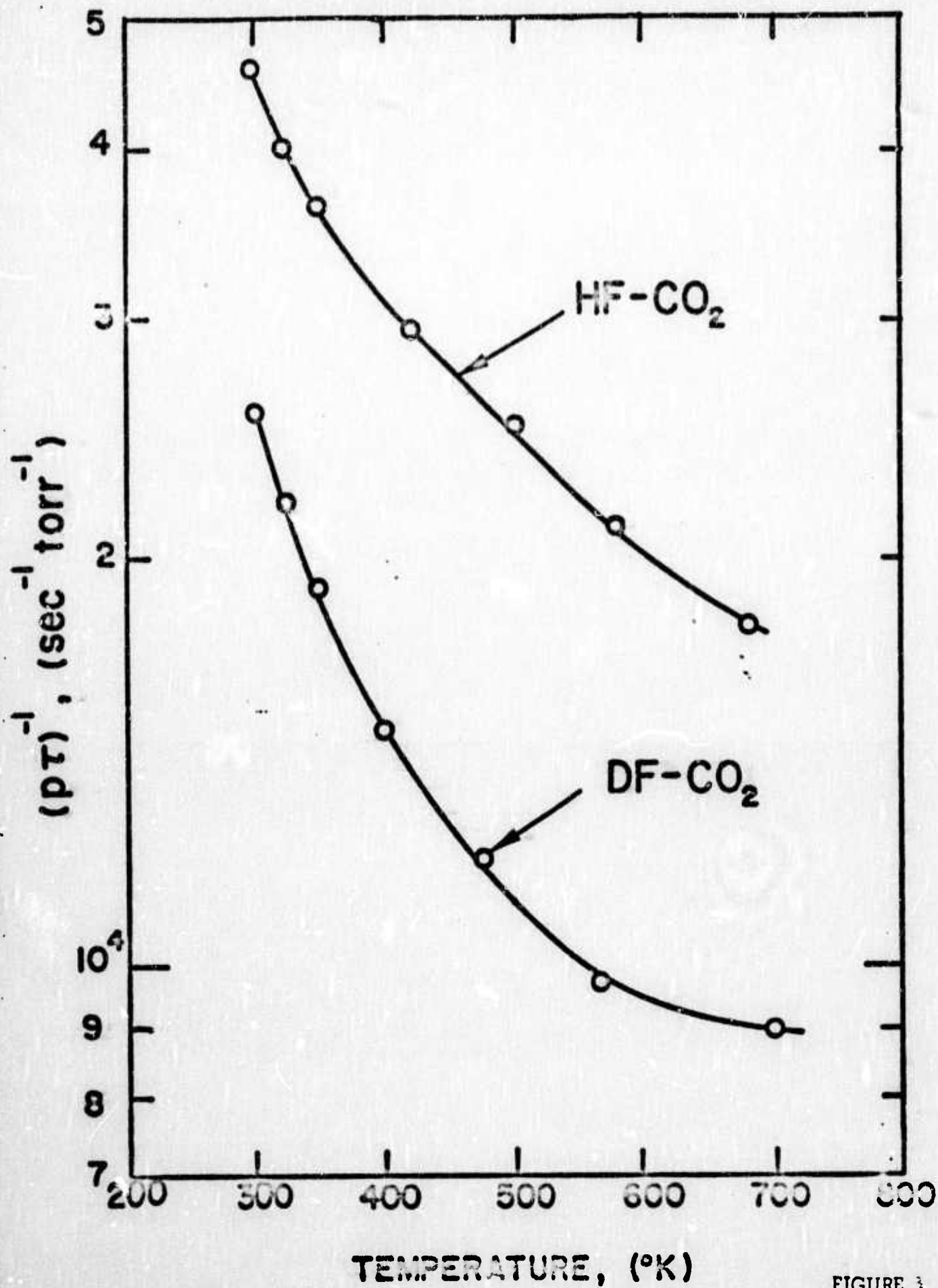


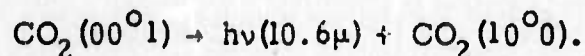
FIGURE 3



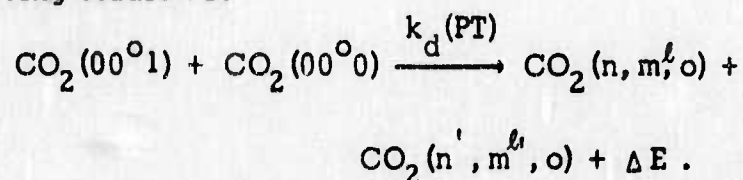
### 3.0 VIBRATIONAL RELAXATION AT HIGH PRESSURES

Professors George J. Wolga and Ross A. McFarlane

3.01 A New experimental method has been developed for the high pressure studies of deactivation of  $\text{CO}_2(00^01)$  by  $\text{CO}_2(00^00)$  and by other molecules. The experimental apparatus is shown in the accompanying figure. Detectors  $D_2$  and  $D_3$  permit the measurement of the time integrated absorbed energy for the pumping process  $\text{CO}_2(00^00) + h\nu(4.3\mu) \rightarrow \text{CO}_2(00^01)$ . The detector  $D_1$  permits measurement of the time integrated  $10\mu$  fluorescence from  $\text{CO}_2(00^01)$  described by



The process being studied is



We shall show in a later report that so long as the collisional relaxation rate  $k_d$  is fast compared to the radiative relaxation of the  $(00^01)$  state, then the rate  $k_d$  at pressure  $P$  is determined relative to  $k_d$  at some reference pressure  $P_0$  where  $k_d$  is known by the relationship

$$\frac{k_d(P)}{k_d(P_0)} = \frac{E_{4.3, \text{abs.}}(P)}{E_{4.3, \text{abs.}}(P_0)} \frac{E_{10.6 \text{ emitted}}(P_0)}{E_{10.6 \text{ emitted}}(P)} \frac{A_{10.6}(P_0)}{A_{10.6}(P)}$$

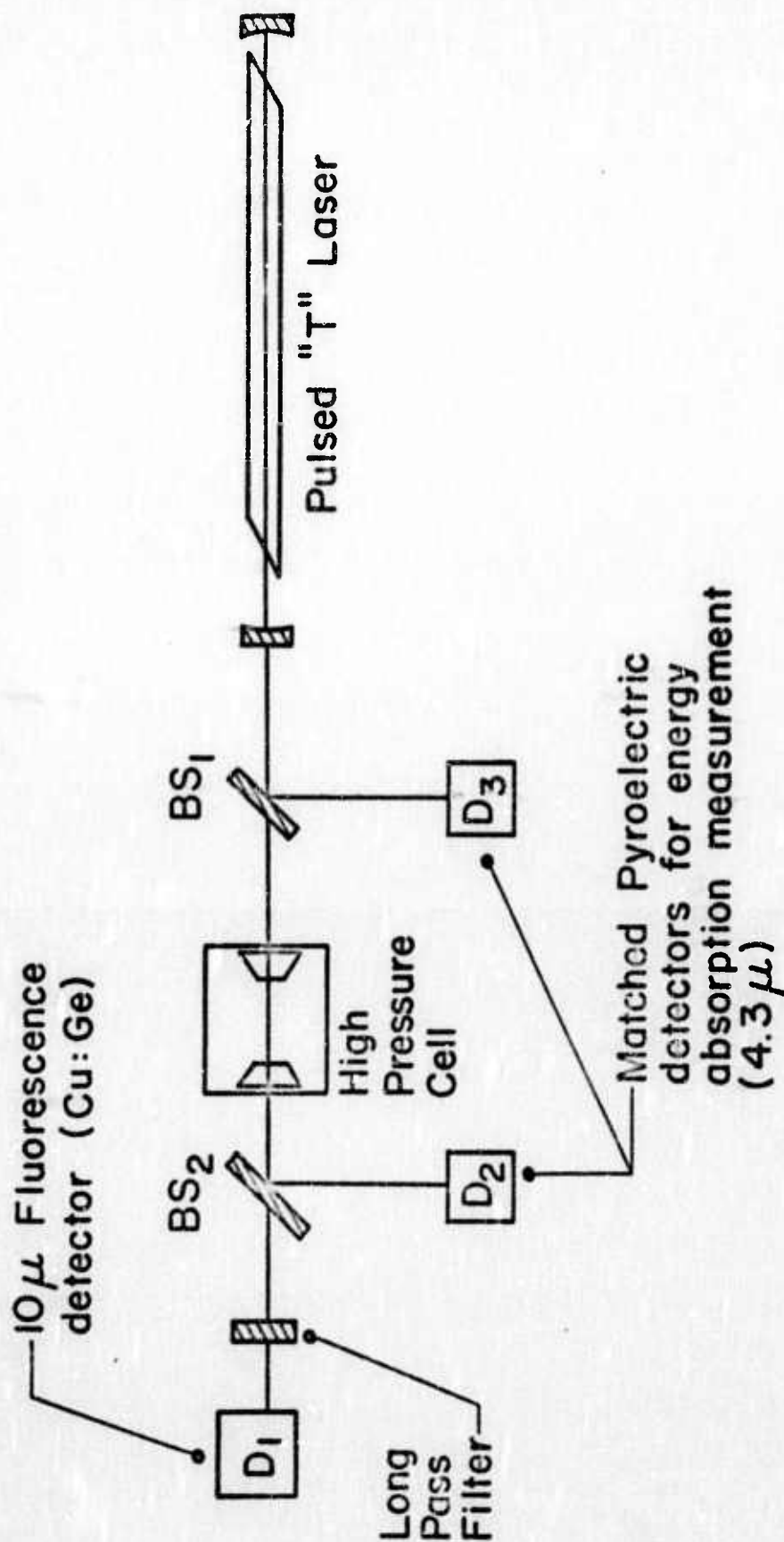
where the E's are the time integrated energies discussed above and the A's are the Einstein A coefficients for the  $10.6\mu$  transition. The advantage of this method over the usual laser induced fluorescence

method is that the  $4.3\mu$  pump pulse need not be short compared to the collisional relaxation time, and much better signal to noise is achieved due to use of the entire pump pulse and large detector load resistors permitted because of the relaxation of the requirement for good time resolution. This method is therefore appropriate for very high pressures where  $k_d$  becomes very large.

We have tested the method in the range 1-10 atmospheres and excellent signal to noise was achieved. Preliminary results are that  $k_d$  increases essentially linearly with pressure up to 75 psia at  $T = 300^\circ\text{K}$ .

3.02 The Spin Flip Raman Laser instrumentation has been purchased (non ARPA funding) and assembled. It is currently being tested with CO laser pump radiation. A TEA HF laser was constructed and output in the  $14\mu$  region from pure rotational transitions was observed. We shall be testing the SFR laser with the  $14\mu$  pump in the near future.

## HIGH PRESSURE RELAXATION EXP.



#### 4.0 CHEMICAL LASER STUDIES

Professors S. H. Bauer, R. A. McFarlane, and G. J. Wolga

##### 4.01 C<sub>2</sub>H<sub>2</sub> + O<sub>2</sub>

###### Introduction:

The exothermic reaction of atomic oxygen with acetylene can provide substantial population of excited vibrational levels of carbon monoxide and as reported for the last period it has been possible to produce a total vibrational inversion for levels  $v = 5$  to  $v = 7$  by preferential collisional relaxation using cold CO.

In addition, spontaneous emission studies which yield the detailed relative vibrational populations have shown that Treanor pumping can lead to partial inversions at higher  $v$  levels for high fuel flows. It remains however to establish that absolute optical gains, though now known to be positive in regions of the flowing system, are sufficiently large to be of utility for laser purposes. These gains must overcome unavoidable losses in a laser resonator just to reach threshold and must be such as to permit in addition significant output coupling.

The present longitudinal flow system is expected to have a distance dependent gain coefficient as determined by the oxygen/C<sub>2</sub>H<sub>2</sub> mixing, time dependent chemistry, vibrational energy transfer and overall relaxation processes. Measurements are being undertaken to determine the net single pass gain of the system at discrete wavelengths under reaction

conditions already known to produce total or partial inversion. The period of this report has been devoted to construction of the necessary instrumentation which includes a single frequency CO laser and the detection and signal handling electronics for gain measurements. A schematic of the system is shown in the figure.

### CO Laser

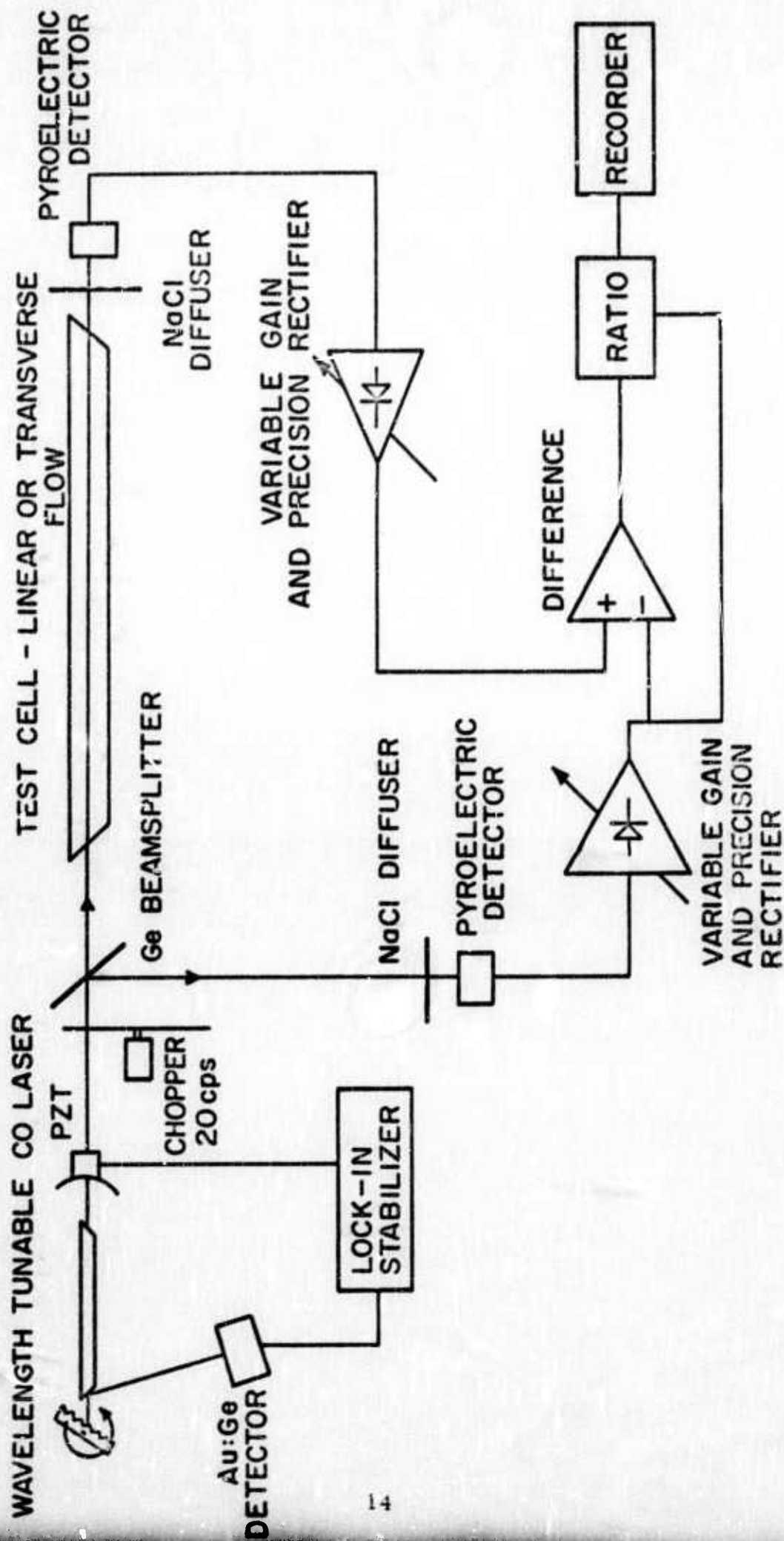
A grating tuned CO laser has been constructed with provision for sealed-off operation. It has been operated with cold water cooling and provision made in the gas handling system for the additions of xenon for closed operation. A current stabilizer has been constructed and placed in use to improve the amplitude stability of the output. During gain measurements the laser will be further stabilized by using a piezoelectric cavity length control to lock onto the center of a particular rotational line.

### Signal Processing

Measurement of single pass gain will be carried out using a pair of matched pyroelectric detectors, one to sample input power and the other to measure power transmitted by the test cell. The laser output is chopped at 20 c.p.s. and the a.c. signals from the detectors are at sufficiently high level to obviate the requirement for phase sensitive detectors. Direct rectification of the a.c. signals to provide a d.c. output proportional to input laser power was not adequately accurate over our range of signal levels and the system is being modified to use precision (.05%) R.M.S.



# GAIN MEASUREMENT SYSTEM



modules to permit detection of gains as low as a few tenths of a percent. The electronic system provides a normalizing function to remove effects due to changes in laser power during a measurement, the final output being

$$V_{\text{out}} = K \frac{P_{\text{out}} - P_{\text{in}}}{P_{\text{in}}}$$

and the constant K will be set to provide a full scale response corresponding to 4% gain.

#### 4.02 C<sub>3</sub>O<sub>2</sub> + O<sub>2</sub>

During the past period we continued to search for an improved synthetic procedure to prepare C<sub>3</sub>O<sub>2</sub> for use in the C<sub>3</sub>O<sub>2</sub>/O<sub>2</sub> electric-pulsed laser. The classic method calls for mixing the dry powers of malonic acid  $\begin{array}{c} \text{HO} \\ \diagdown \\ \text{C} \\ \diagup \\ \text{O} \end{array} - \text{CH}_2 - \begin{array}{c} \text{O} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{OH} \end{array}$  with phosphorous pentoxide (P<sub>2</sub>O<sub>5</sub>), in 1/10 ratio, and heating the mixture to 150°C in the absence of any solvent. The yield of that procedure is ≈ 10%. In a series of experiments, based on extensive discussions with organic chemists, we tested various solvents, hoping to facilitate direct contact between the malonic acid and P<sub>2</sub>O<sub>5</sub> at the molecular scale. Tests were run between temperature 0°C and 60°C. None yielded any substantial amounts of the desired gas. However, all gave evidence of extensive reaction followed by rapid polymerization. The dehydrohalogenation of malonyl dichloride, utilizing basic alumina or trialkylamines as HCl abstracting agents, was also explored as a possible synthetic route, but with no success. We are now convinced that

solvents of any kind should be avoided because these provide the best conditions for  $C_3O_2$  polymerization.

Optimum yields are obtained by: (a) fine grinding of the malonic acid and thorough mixing with the  $P_2O_5$ ; (b) maintaining the reaction temperature at about  $50^\circ C$ ; (c) running a slow stream of helium through the mixture to displace the  $C_3O_2$  from the tacky reaction products as rapidly as possible; (d) stirring continuously to break up the tacky clumps of phosphoric acid coated crystals of malonic acid. Further exploration are in progress for improved reactor design, and possible admixing of acidic dehydrating agents which will reduce the tackiness of the products, and thus permit more complete reaction.

With respect to our laser radiation studies, emissions between  $5.1 - 5.4 \mu$ , corresponding to transitions in CO from  $v' - v''$  (1--9) to (6-5) have been observed, following pulsed electrical discharge through gaseous mixture of  $C_3O_2$ ,  $O_2$  and He using two types of laser tubes: the one meter, 2.5 cm I.D. unit, with ring electrodes, and a 1 meter, 6 cm I.D. tube in a TEA configuration. Maximum lasing signal was obtained in the former when a 4.56 nf capacitor was discharged, at 11 Kv, through a mixture of about 0.5 torr  $C_3O_2$ , 1.2 torr  $O_2$ , and 4.1 torr He. In the TEA configuration lasing intensities were an order of magnitude higher than in the ring electrode tube. Lasing was initiated with a 14.4 nf capacitor, discharged at 20 Kv, through 2 torr of  $C_3O_2$ , 13 torr  $O_2$ , with no added helium. The need for an efficient preparative method for  $C_3O_2$  is

obvious since under our operating conditions, at a partial pressure of 2 torr,  $C_3O_2$  is consumed at the rate of about 2 grams per minute.

Our objectives are to obtain estimates of the vibrational state population of the nascent CO, and to accumulate data on the effect of operating variables to provide a basis for developing a more complete mechanism for the lasing reaction.

#### 4.03 $CS_2 + O$

Parallel with the above development, the formulation of a complete kinetic model for the  $CS_2 + O$  reaction is continuing. To date we have carefully reviewed all the models that have been proposed and concluded that these were grossly incomplete with respect to the reactions considered and inadequately documented with respect to the specific rate constants selected for insertion in the kinetics programs. Also they were generally run under the assumption of isothermal conditions, which is far from realistic. Our present computer program permits the solution of the simultaneous equations under totally or partially adiabatic constraints (but, we did not specifically introduce a thermal conductivity term). Also, for practical purposes, we have exhausted the literature on  $CS_2$  and COS pyrolysis, photolysis and oxidation. Now, the numerous proposed mechanisms have to be sifted before we can make a final selection of the steps that are dominant during laser operation, and of the corresponding rate constants. Incidentally, up to now the possible roles of  $CS_3$ ,  $O_3$ ,  $S_2O$  and in particular  $CS^{(v)}$  in controlling the mechanism have not been adequately

considered. This we are in the process of doing. It seems that  $CS_3$  is a short lived but very reactive intermediate, and may play an important kinetic role. We hope that within the next two months to have made a series of test runs with our program, in which radiative lifetimes,  $v-v$  transfer probabilities, and the exploration of the role of  $CS^{(v)}$  have been introduced.



## 5.0 MOLECULAR RELAXATION VIA ATOMIC COLLISIONS

Professors S. H. Bauer, G. J. Wolga, and R. A. McFarlane

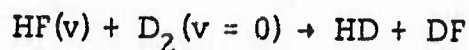
5.01 Testing of the apparatus for the study of the deactivation of HF/DF( $v = 1$ ) by H, D, F, O, N has been completed. The HF/DF pump laser has been optimized for  $v = 1 \rightarrow 0$  transitions and laser induced fluorescence with good signal to noise was observed from HF in the test cell using borrowed R-branch filters. Appropriate blocking filters are scheduled for delivery within two weeks after which data taking will commence. The atom concentration measuring apparatus is in operation. A vacuum blower is being installed in the flow system to increase the atom flow velocities.

5.02 Testing of the apparatus for the study of the deactivation of  $\text{CO}_2(00^01)$  by H, D, F, D, N is in progress. The atom concentration measuring apparatus is in operation. The TEA HBr laser for pumping the laser induced fluorescence experiment is in operation but we are awaiting delivery of a diffraction grating to select a particular HBr pump line in the  $v = 2 \rightarrow 1$  band. Data taking will commence in the near future.

## 6.0 VIBRATION ENHANCED CHEMICAL EXCHANGE REACTIONS

Professor G. J. Wolga

6.01 The effect of the vibrational excitation of HF(v) on the rate of the simple atom exchange reaction



is being studied. A TEA HF laser emitting predominantly on  $v = 3 \rightarrow 2$ ,  $2 \rightarrow 1$ , and  $1 \rightarrow 0$  bands was optimized for maximum overlap in time of the emissions most effective in pumping HF to the  $v = 3$  state by successive absorptions on vibrational-rotational transitions. This laser is being used to optically pump HF in a cell also containing  $\text{D}_2$ . An identical, companion cell is filled with the same gas mixture and is used as a control. After a period of irradiation with the laser both cells are separately analyzed using a mass spectrometer for the HD content. To date reaction enhancement, i.e., conversion of HD by the reaction, of up to 20 percent has been observed. Parametric studies of the enhancement are currently in progress.